Comparison of Perturbative and Variational Treatments of Molecular Vibrations: Application to the Vibrational Spectrum of HFCO up to 8000 cm^{-1}[†]

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We calculated highly excited states of the HFCO molecule, comparing results from two methods. In the first method, Van Vleck perturbation theory is used to transform away all off-diagonal couplings except those between nearly degenerate states. This perturbative transformation leads to a matrix representation where eigenvalues are obtained with relatively small matrices. In the second method, variational eigenvalues are obtained by combining the Jacobi−Wilson approach with the block-Davidson scheme. The key ingredient here is a prediagonalized-perturbative scheme applied to a subspace of a curvilinear normal-mode basis set. Comparisons of the two methods provide a critical test of the less time-consuming perturbation theory. Two different coordinate sets are used to test the sensitivity of the results to coordinate choice. Perturbation theory also requires a polynomial fit to the potential. The implications of this restriction are investigated.

I. Introduction

High-resolution spectroscopy provides fully resolved spectra of highly excited systems such as H_2CO, HFCO,[1−3] DFCO,[4,5] CF_3H,[6−11] CH_3OH,[12] or C_6H_6 [13−15] to cite a few examples. However, such accurate data cannot be fully understood using basic models. Consequently, quantum simulations are required to help analyze these accurate spectroscopic data. For this reason, considerable research has been carried out over the years to develop both better ab initio quantum methods for calculating a potential energy surface (PES) and more efficient numerical methods for solving the rovibrational Schrödinger equation. The present study focuses on the latter. Prominent among these studies are several pioneering studies of the Light group,[16−22] to which this volume is dedicated.

A crucial step in a variational calculation is the choice of coordinates that describe the atomic motion. The rectilinear normal modes constitute the most popular set of coordinates to describe the motion of the atoms near the equilibrium geometry. At least two very interesting quantum codes (Multimode[23−25] and Conviv[26−28]) using such a rectilinear description have been developed to study moderately excited rovibrational spectra of molecular systems. Such methods are based on a preliminary variational self-consistent field (VSCF)[23,25] or vibrational multiconfigurational self-consistent field (VMCSCF)[26] treatment of the working basis set in order to reduce its dimension thereby allowing the study of large systems. Calculations with rectilinear coordinates can be extremely hard to converge for highly excited states. In such a case, a curvilinear description has to be adopted. However, the kinetic energy operator (KEO) expression can be intricate and it can be difficult to evaluate the results of it acting

on an efficient basis set. One elegant and efficient way consists of performing a Taylor series development of the G matrix element of the KEO. Such an approach has been intensively applied by Sibert and co-workers in canonical Van Vleck perturbation theory (CVPT).[29−34] Recently, it has also been used by Pouchan and co-workers[35−37] to calculate low-excited vibrational spectrum of large isolated or solvated molecules. For large amplitude motions, such a development might be less efficient; in such a case, the exact KEO has to be used. Luckhaus[38] has shown that such complex KEOs can be evaluated exactly using the discrete variable representation (DVR).[17,18] Finally, an underlying pseudo-spectral scheme can help to apply such an intricate operator on a vector of the working basis set.

We believe that the numerical methods used to calculate rovibrational spectra should provide not only the eigenvalues but also the eigenstates or, at least, their main projections on some given states. This point is crucial if quantum simulations are to help with the assignment of experimental spectra. Unfortunately, the dimension of the direct-product basis set dramatically increases both as the number of atoms increases and as the energy of the states to be calculated increases. For this reason, many numerical methods try to decrease the dimension of the working basis set in which the rovibrational Hamiltonian is diagonalized. A VSCF[23,25] or VMCSCF[26] treatment helps this decrease by defining a more adapted basis set. The CVPT method[29] applies an efficient perturbative treatment to drastically decrease the dimension of the basis set in which the Hamiltonian is diagonalized. This method will be described in section IV. Pouchan and co-workers[35−37] select an adapted active space in which the Hamiltonian is diagonalized to provide fundamental and low-excited combination bands for large systems. This approach also combines a variational

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approach with a perturbative treatment. A great number of purely variational methods have been developed that use sophisticated methods to extract highly excited states from a huge primitive basis set. In such a case, a popular method is the Lanczos algorithm.[39] As the convergence of the Lanczos scheme becomes very slow for the denser part of the spectrum, that is, at higher energies, spectral Lanczos algorithms[40] can greatly improve the convergence. This consists of using, in the Lanczos recursions, another operator f(**H**) whose spectrum is strongly dilated around some reference energy. Such an approach is efficient[41−43] but is CPU time-consuming because computing f(**H**) is in general very expensive if the state density increases. Recently, Huang and Carrington proposed the PIST[44] (preconditioned inexact spectral transform) method that uses an iterative linear solver to compute approximate Lanczos vectors; the resulting Hamiltonian matrix is diagonalized in this basis set. This approach has been combined with several preconditioners.[45,46] These preconditioners include a phase space optimization DVR, an optimal separation basis, and Wyatt preconditioning. Bian and Poirier[46] established the great accuracy and efficiency of this very sophisticated approach by computing highly excited vibrational bands of HOCl. Lee and Light proposed an interesting algorithm that uses an energy selected basis set combined with an iterative solution to calculate the eigenvalues and eigenvectors of highly excited triatomics[47] and tetra-atomics.[48] Several groups have also established the great utility of methods based on the Davidson algorithm[49] to extract eigenvalues and eigenvectors from a huge basis set.[50−55] One of these approaches is discussed in section III.

In this paper, we will compare two methods: they are the perturbative CVPT[29] method and the Jacobi−Wilson (JW)[52−55] variational approach. In the first method, eigenvalues are obtained via the Van Vleck perturbation theory which is used to transform away all off-diagonal coupling except those between degenerate states. This perturbative transformation leads to a matrix representation where eigenvalues are obtained with relatively small matrices. Such an approach has been successfully applied to compute vibrational spectra of a large variety of molecules, H_2CO,[29] CF_4,[31] CH_3OH,[32] and CX_3H (X = Br, F)[33,34] to cite a few examples. In the second method, variational eigenvalues and eigenvectors are obtained by combining the JW approach with the block-Davidson scheme.[52−55] The key ingredient is a prediagonalized scheme applied to a subspace of curvilinear normal-mode basis functions. These two strategies are totally different, and for this reason, it is interesting to compare the results obtained by them. Moreover, the origins of the inaccuracies of these two methods are expected to be different, so these two methods can be complementary.

These two methods are applied to HFCO, a good candidate for testing the efficiency of the two methods for at least two reasons. First, this system is of interest because the energy flow is found to be strongly state specific when the out-of-plane mode is highly excited. In their stimulated emission pumping experiments of the unimolecular dissociation of HFCO into HF + CO, Choi and Moore[1−3] were able to assign $(0, n_2, 0, 0, 0, n_6, J, K_a, K_c)$ levels for $n_6 = 14, 16, 18,$ and 20 well above the dissociation threshold. Moore and co-workers suggest that IVR in this system cannot be explained by statistical theories: they consider that the energy flow through this molecule from the initially excited out-of-plane mode is highly selective. Sophisticated quantum numerical simulations are required to explain why the C=O stretching mode (ν_2) and the C−H out-of-plane mode (ν_6) seem to be decoupled from the other modes when the excitation energy in the out-of-plane mode is large. To investigate the nature of the energy flow in HFCO,[56,57] a global PES has been calculated by Kato and co-workers[58] to describe both geometries near equilibrium and the dissociation path of this molecule HFCO → HF + CO. They built a global analytical PES for the ground state using about 4000 ab initio points computed at the RHF/MP2 level. The form of this PES is not adapted to the CVPT method. We therefore fit the PES in a polynomial form. The error generated by this fit is estimated and discussed. This point is germane because any analytical PES is fitted: this step always introduces some error which is not usually quantified. Consequently, this molecule is a good candidate to test different methods for calculating either combination modes $|v_1, ..., v_6\rangle$ or highly excited overtones $|nv_i\rangle$.

The outline of this article is as follows. In section II, we present the HFCO system and the two sets of coordinates used to describe its internal deformation. These two sets of coordinates are identical for in-plane geometries, but differ for out-of-plane geometries. In section III, the variational JW method coupled to an efficient Davidson scheme is reviewed and applied to HFCO. In section IV, CVPT is applied to HFCO. Section V is devoted to the analysis of the error generated by the two polynomial fits of the PES. The spectra obtained with both the CVPT method and the JW variational approach are compared in section VI. The sensitivity of the results to coordinate choice is also discussed. Section VII concludes and gives some perspectives.

II. Choice of Coordinates

Since the choice of coordinates can strongly influence the convergence of both variational[59] and perturbative calculations,[30] in this study, we will obtain results for two sets of coordinates. A comparison of the results will allow us to evaluate the influence of the choice of coordinates on the efficiency of the methods. In general, it is desirable to develop methods for solving the nuclear Schrödinger equation that are not overly dependent on the choice of the set of coordinates. One wants to develop methods that are flexible enough that they will work for an entire family of coordinates in order to describe a large variety of systems in an optimal way. Although the two sets of coordinates used in this study differ only for out-of-plane geometries, this difference leads to notable differences in the couplings between the coordinates.

The first set of coordinates is the polyspherical set[60] generated by the three vectors $\vec{R}_3 = \overrightarrow{CO}$, $\vec{R}_2 = \overrightarrow{CF}$, and $\vec{R}_1 = \overrightarrow{CH}$. In this parametrization, which has recently been reviewed,[61,62] the system is described by the spherical coordinates $(R_i, \vartheta_i, \varphi_i)$ of the three vectors $\vec{R}_i$ ($i = 1, 2, 3$) in a coordinate system with the C atom at the origin, the O atom on the positive z-axis, and the F atom lying in the xz-plane with $x > 0$. It results in the following internal coordinates: three radial coordinates (R_{CO}, R_{CF}, R_{CH}), two in-plane coordinates ($\vartheta_1 = \angle HCO$, $\vartheta_2 = \angle FCO$), and one dihedral coordinate $\phi = \varphi_1$. We also denote the first set as the ϕ set, to distinguish it from the second set, the δ set, previously used by Burleigh et al. to study H_2CO.[30] Here, the C atom is at the origin, but the O atom lies on the positive x-axis. The vectors $\overrightarrow{CF}$ and $\overrightarrow{CH}$ are parametrized by their spherical coordinates (R_{CF}, α_{CF}, β_{CF}; R_{CH}, α_{CH}, β_{CH}) measured in a coordinate system such that $\alpha_{CF} = \alpha_{CH} = \delta$. The δ set consists of three radial coordinates (R_{CO}, R_{CF}, R_{CH}) and three angular coordinates (β_{CH}, β_{CF}, δ). The in-plane coordinates are similar in these two parametrizations for planar geometries, while the out-of-plane coordinates (ϕ and δ) are different. For instance, ϕ is set to π while δ is equal to $\pi/2$ for the planar equilibrium geometry.

TABLE 1: Experimental Fundamental Frequencies[1] of HFCO Expressed in cm^{-1}

mode	frequency (cm^{-1})	symmetry	description
1	2981	A′	CH stretch
2	1837	A′	CO stretch
3	1347	A′	HCO bend
4	1065	A′	CF stretch
5	662	A′	FCO bend
6	1011	A″	out-of-plane bend

We use the global PES developed by Kato and co-workers.[58] The normal-mode frequencies obtained with this PES are provided in Table 1. These frequencies will aid in the prediction of the kinds of resonances that can occur for this molecule.

III. Variational Jacobi−Wilson Method Coupled with a Davidson Scheme

The recently developed JW method has been applied to HFCO.[54] As the full details of this method are given by Leforestier et al.,[63] we will only outline the key points here. Starting from a description with a set of six polyspherical coordinates,[61,62] denoted $\{q_n, n = 1, ..., 6\}$ corresponding to a Jacobi vector parametrization of the system,[54,55] a set of *curvilinear* normal coordinates, denoted $\{Q_\alpha, \alpha = 1, ..., 6\}$, is introduced to calculate the excitation vibrational spectrum. These *curvilinear* normal coordinates are provided by the FG method of Wilson,[64] that is

$$Q_\alpha = \sum_{n=1}^{6} L_{\alpha n}^{-1} q_n \qquad (1)$$

This method combines the simplicity[60,65,66] of the exact KEO expressed in terms of polyspherical coordinates with the efficiency of the Wilson normal-mode approach.

Our corresponding basis functions are eigenfunctions of six uncoupled harmonic oscillators describing the curvilinear normal coordinates. This normal-mode basis can be refined further by including the diagonal anharmonicities.[63] Specifically, the molecular basis set $\mathscr{B}$ is thus spanned by the product functions $|v_1, ..., v_6\rangle^o$ where v_i corresponds to the occupation number of the anharmonic oscillator describing the normal-mode Q_i. This basis $\mathscr{B}$ is restricted by an energy cutoff

$$\text{If } E_{v_1...v_6}^{0} \leq E_{\text{max}}^{0}(|v_1, ..., v_6\rangle)$$

$$|v_1, ..., v_6\rangle^0 \in \mathscr{B} \qquad (2)$$

One can also impose some constraints ($n_\alpha \leq N_\alpha$) on the maximum occupation number of each mode. To selectively study one state or a series of coupled states, one can define a more specific basis set. For instance, highly excited overtones of the out-of-plane $|nv_6\rangle$ ($n \leq 10$) have been recently calculated[55] by adding a second energy criterion limiting the energy in the in-plane modes. This allows us to use a more adapted working basis set.

A pertinent feature of the method is the presence of an underlying pseudo-spectral scheme, allowing very large molecular basis sets to be used by means of *direct* iterative methods. That is, one defines a 6D grid, $\mathscr{G}$, subject to an energy cutoff: $Q_{1a} \times ... \times Q_{6f} \in \mathscr{G}$ if $V_{a...f} \leq E_G$. By using a grid cutoff larger than the basis cutoff, $E_G = \eta E_{\text{max}}^{0}(|v_1, ..., v_6\rangle)$ ($\eta > 1$), one can enforce dealiasing.[67] For the calculations presented below, we have used an η value of 1.2. The presence of this pseudo-spectral scheme allows one to use any kind of PES expression. This constitutes an central advantage of this method. However, the

use of this underlying pseudo-spectral scheme increases the CPU time and the memory required.

An efficient Davidson[49] scheme is employed to calculate the eigenvectors and eigenvalues of the system.[52−55] The accuracy of this method is controlled during the iterative Davidson process by evaluating the residual $||(H - E_M)\Psi_M||$ where (E_M, Ψ_M) denote the estimated energy and eigenvector obtained after M Davidson iterations, respectively. We have established elsewhere[54,55] that the residual is a measure of the quality of the eigenvector and eigenenergy obtained, even for highly excited overtones.[55] To obtain accurate results, eigenvectors and eigenenergies are considered as converged when their residual is smaller or equal than 1 cm^{-1}. It results in an accuracy better than about 0.1 cm^{-1} for energies smaller than 8000 cm^{-1}. Consequently, the unique origin of the inaccuracy of this variational method comes from the finite dimension of the working basis set.

The calculation of states $|v_1, ..., v_6\rangle$ such that $v_i \leq 3$ has been obtained in a basis set containing all the zero-order states, $|v_1, ..., v_6\rangle^0$, whose zero-order excitation energy was smaller than $E_{\text{max}}^{0}(|v_1, ..., v_6\rangle) = 28\,000$ cm^{-1} while the quantum number v_i was smaller or equal to 10. It results in a working basis containing about 100 000 states and the use of a grid of about 1.8×10^6 points. For combination states $|v_1, ..., v_6\rangle$ with one quantum number equal to four and for overtones states $|nv_i\rangle$, a specific basis set has been built to improve the accuracy of the variational calculation. For instance, in calculating the out-of-plane $|nv_6\rangle$, a third parameter has been introduced: the maximum allowed excitation energy in the in-plane modes ($E_{\text{max}}^{0}(|v_1, ..., v_5\rangle)$), in order to allow a larger energy in the out-of-plane mode. These overtones states, $|nv_6\rangle$, have been obtained in a basis set such that $E_{\text{max}}^{0}(|v_1, ..., v_6\rangle)$ and $E_{\text{max}}^{0}(|v_1, ..., v_5\rangle)$ were set to 35 500 and 25 500 cm^{-1}, respectively, while the in-plane quantum numbers v_i ($i = 1, ..., 5$) were smaller or equal to 8. It results in a 150 000 state basis set adapted to compute states with large excitation in mode 6. Consequently, the JW method coupled to a Davidson scheme has been used to calculate all the overtones states $|nv_i\rangle$ associated with energies smaller than 8000 cm^{-1} and all the combination states $|v_1, ..., v_6\rangle$ associated with energies smaller than 7000 cm^{-1} and such that $v_i \leq 4$. For these states, we can consider that the error of the variational energies near 3000 and 7000 cm^{-1} is smaller than 0.1 cm^{-1} and about 3 cm^{-1}, respectively. The comparison with the perturbative calculation is limited to these states, that is, combination states with $v_i \leq 4$ and overtones states, because we are able to estimate the accuracy of the energies provided by this variational method. This is important because these variational energies will be compared to perturbative energies provided by CVPT.

IV. CVPT Perturbative Theory

The application of Van Vleck perturbation theory to the HFCO presents three challenges. First, the molecule dissociates at relatively low energy, and one expects the perturbation theory to fail as one approaches this energy. Second, in contrast to our recent work on SCCl$_2$,[68] the normal-mode frequencies, given in Table 1, are such that there is no easily identifiable polyad structure. This structure is essential if one is to construct a block-diagonal Hamiltonian and thereby reduce the dimensionality of the Hamiltonian. Nonetheless, perturbation theory can be used to "precondition" the Hamiltonian so that the Hamiltonian matrix can be diagonalized using a relatively small basis set. Third, the potential needs to be reexpressed as a Taylor series expansion in the normal coordinates in order to implement the Van Vleck transformations.

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TABLE 2: List of Resonances that Are Included in the Perturbative Hamiltonian K

Δn_1	Δn_2	Δn_3	Δn_4	Δn_4	Δn_6
-1	1	0	1	0	0
1	-1	-1	0	0	0
0	0	1	0	1	-2
0	0	1	-2	1	0
0	0	0	-2	0	2
0	-1	1	1	-1	0
1	0	-1	-1	-1	0
1	0	0	-1	0	-2
1	-1	0	0	-2	0
1	0	0	-3	0	0
-1	2	0	0	-1	0

In this approach, we also use curvilinear normal coordinates (cf. eq 1). Here, the Hamiltonian, with volume element $dQ_1 dQ_2 \cdots$, takes the simple form

$$H = \frac{1}{2} P^T G P + V'(\mathbf{Q}) + V(\mathbf{Q}) \qquad (3)$$

where the components of $\mathbf{P}$ are $P_k = -i\hbar \partial/\partial Q_k$, the momentum conjugate to Q_k. The **G**-matrix elements and $V'(\mathbf{Q})$ are expanded in a Taylor series about the equilibrium configuration through sixth and fourth order, respectively, using standard analytical expressions for these terms.[69] The Hamiltonian is expanded as

$$H = \sum_{k=0}^{N} \lambda^k H^{(k)} \qquad (4)$$

where λ is the perturbation parameter. The potential and kinetic terms of the order $k + 2$ are included in $H^{(k)}$, and the $V'(\mathbf{Q})$ terms of the order k are included in $H^{(k)}$. This Hamiltonian is subsequently expressed in terms of harmonic oscillator raising and lowering operators.

The Van Vleck transformations are accomplished via a succession of unitary transformations

$$T_k = \exp\{i\lambda^k [S^{(k)},]\} \qquad (5)$$

applied to the original Hamiltonian to give

$$K = T_N \cdots T_2 T_1 H \qquad (6)$$

where the $S^{(k)}$ are chosen such that K has the desired form. Normally, one attempts to transform to a K such that, when written as a matrix, it is block-diagonal. Given the low symmetry and distribution of normal-mode frequencies, this approach was not successful. In a recent study of CHF$_3$, Ramesh et al.[33] defined several polyad numbers and then retained all coupling terms that conserve any one of the polyad numbers. Here, we pursue a closely related approach; we transform K so that it only includes diagonal contributions and a select set of resonance interactions. Equivalently, the perturbative results are obtained by transforming away all nonresonance terms in the Hamiltonian. Specifically, a resonance term is defined as any term that couples two states whose absolute difference in zero-order energies

$$|E_v^0 - E_{v'}^0| = |\sum_i \Delta v_i \omega_i| \qquad (7)$$

is less than or equal to an energy cutoff $E_{\text{cut}}(k)$ where k is the order of the coupling terms. Here ω_i are the harmonic frequencies. The cutoff values we have used are 350, 105, 60, 50, and 15 cm^{-1} respectively for $k = 3-7$. These cutoff values lead to 35 resonance terms in the transformed Hamiltonian. Table 2
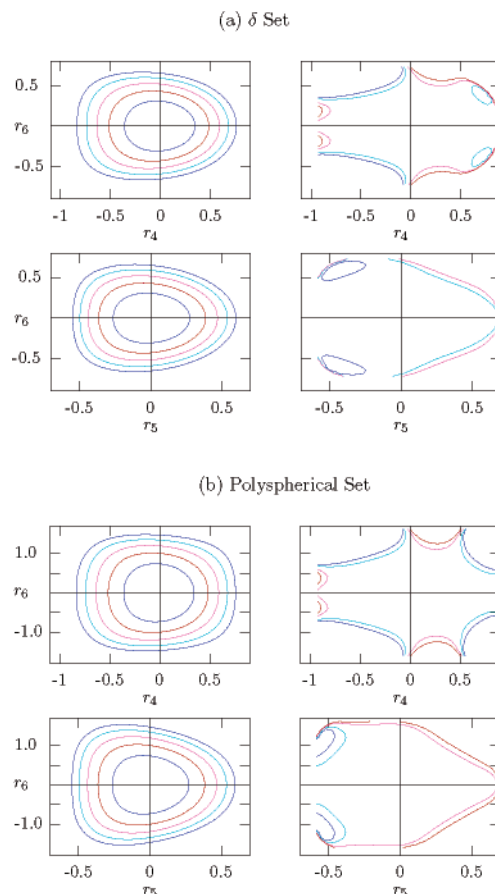

Figure 1. Select 2D equipotential contour plots in (a) δ set and (b) ϕ set of coordinates. The coordinates $\{r_4, r_5, r_6\}$ are extension coordinates corresponding to $\{\beta_{\text{CH}}, \beta_{\text{CF}}, \delta\}$ for the δ set and $\{\vartheta_1, \vartheta_2, \phi\}$ for the ϕ set, respectively. The fit to the Kato potential is shown on the left; the difference between the potential and the corresponding polynomial fit is plotted on the right. On left-hand side, the contour lines are placed at 4000, 8000, ..., 20 000 cm^{-1}, and on the right-hand side, they are placed at -200, -100, 100, and 200 cm^{-1}.

includes a list of the resonances that arise at third and fourth order in the coupling. The first resonance of Table 2 describes the $\omega_1 \approx \omega_2 + \omega_4$ resonance condition. Consequently, terms of the form $a_1 a_2^\dagger a_4^\dagger$ (as well as their higher order analogues such as $a_1 a_1 a_2^\dagger a_2^\dagger a_4^\dagger a_4^\dagger$) are included in the transformed Hamiltonian K.

The Kato potential is not in a form that is amenable to CVPT. More generally, a factorized form of the Hamiltonian (i.e., $H = \sum_{i=1}^{N_{\text{term}}} \prod_{j=1}^{N_{\text{mode}}} f_{ij}(Q_j)$) is required by many efficient numerical methods such as CVPT,[70] multiconfiguration time dependent Hartree (MCTDH),[71] and VMSCF schemes.[26] Such expressions significantly reduce the core memory required and allow one to study larger and more excited systems. However, a global PES which is not given in a factorized form has to be fitted to be used by these methods. Here, it must be reexpressed as a polynomial expansion in the normal coordinates. In principle, this is straightforward, however in practice it presents several numerical challenges. One needs high-order polynomial expansions to have a faithful representation of the potential up to 8000 cm^{-1} above the zero-point energy.

A standard way to improve the convergence of the expansion is to carry out the expansions in internal coordinates using Simons−Parr−Finlan coordinates $\rho_i = r_{ei}r_i/(r_i + r_{ei})$ to describe the stretches. Here, r_i and r_{ei} are the stretch extension coordinate and equilibrium bond length, respectively. Even with this coordinate choice, to achieve the necessary accuracy, our
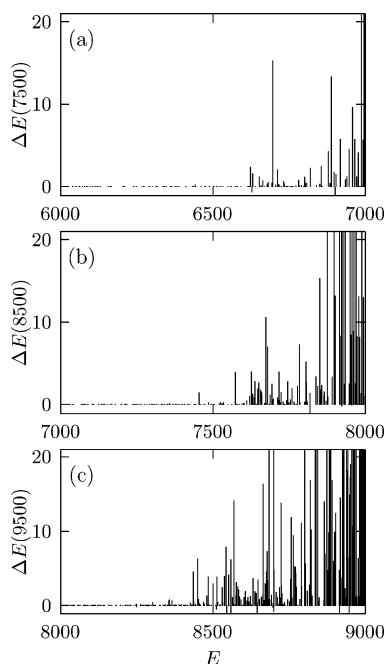
Figure 2. Plots of the energy difference $\Delta E(E_{max}^0)$ vs the corresponding eigenvalues E, for the eighth-order perturbative results using the δ set of coordinates. Here, $\Delta E(E_{max}^0)$ is the difference between an eigenvalue obtained with the basis defined by E_{max}^0, the maximum harmonic energy allowed for a basis function in cm^{-1} and a converged eigenvalue. The value of E_{max}^0 is 7500, 8500, and 9500 cm^{-1} in (a), (b), and (c), respectively. The variationally converged numbers are obtained with $E_{max}^0 = 10\,500\ cm^{-1}$. This latter basis set consists of a modest number of 1454 basis functions.

potential expansions include select terms up to tenth order for both the ϕ and δ sets of coordinates.

In an attempt to determine the Taylor series expansion coefficients, we found that we could only reliably calculate up to sixth-order derivatives. Above this order, numerical instabilities lead to fluctuations in the values of the derivatives obtained via finite differentiation, regardless of the number of points used. The higher order contributions to the potential were determined via least-squares fitting of ΔV, where ΔV is the difference between the full potential and our sixth-order expansion of it. The Taylor series expansion of the potential includes up to four-body terms. The least-squares fit expansion includes only one-body terms.

Figure 1 shows equipotential energy contours for our fit potentials for the (a) δ set and (b) ϕ set. Also shown are the differences between the fit potential and the Kato potential. The results for the plots with respect to other coordinates show qualitatively similar agreement. The plots clearly show that the two-body contribution to the fit potential is in excellent agreement with the Kato potential for energies up to at least 12 000 cm^{-1}. Results for the ϕ and δ sets, although different, do not appear to differ in the extent of the potential coupling. Further tests of the agreement will come from comparison of variational results obtained for the Kato surface and the fits to this surface which are described in the following section.

To obtain eigenvalues associated with the potentials just described, we carry out the perturbative transformations and then diagonalize the Hamiltonian in an appropriate basis set $\mathscr{B}$. Our Hamiltonian allows for most of the plausible resonance interactions and is, therefore, not block-diagonal. As in the variational calculation, $\mathscr{B}$ is restricted by the energy cutoff described by eq 2. We check for convergence by increasing the energy E_{max}^0 and observing how the eigenvalues change.
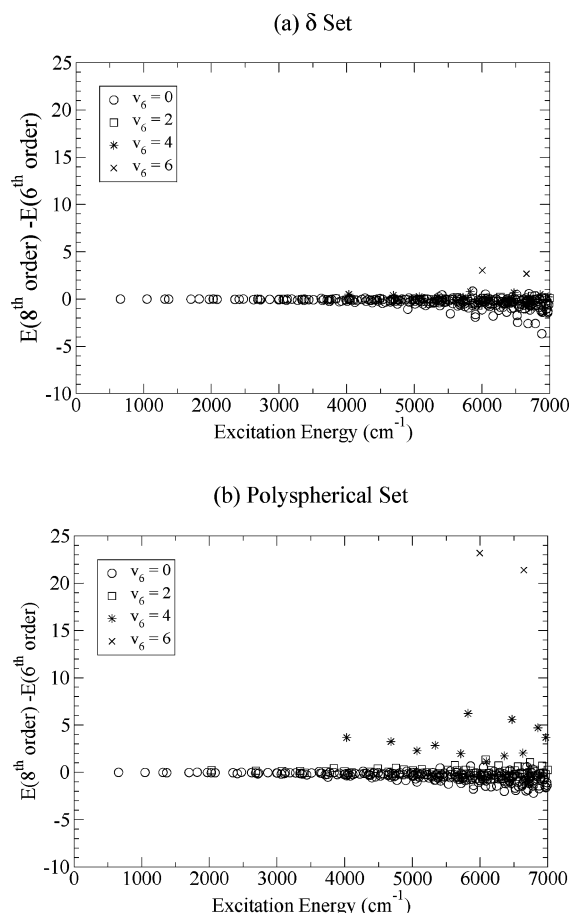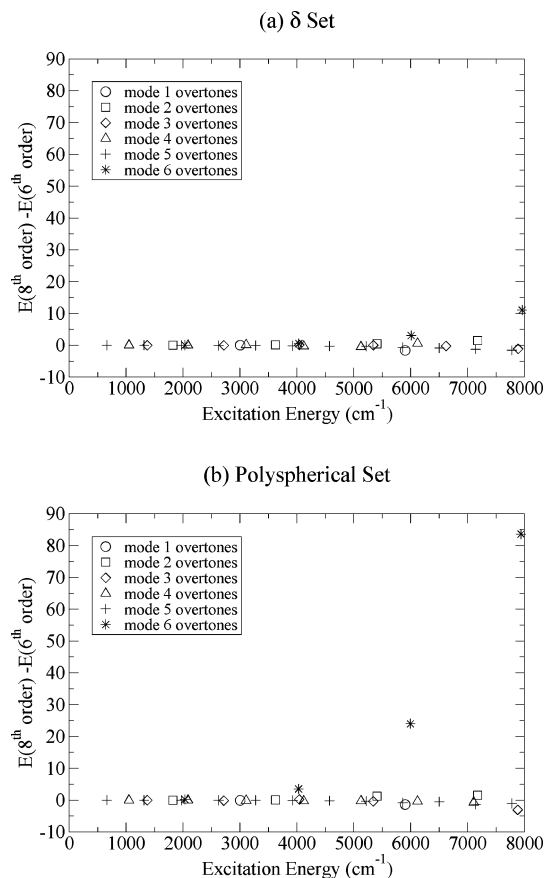

Figure 3. Difference between eighth- and sixth-order perturbative energies, E(eighth order) $-$ E(sixth order) plotted as a function of E(eighth order) with energies expressed in cm^{-1} when the PES is fit with (a) the δ set and (b) the ϕ set of coordinates. Here, v_6 denotes the quantum number of mode 6, that is, the out-of-plane mode.

The significant feature to note in Figure 2 is that as E_{max}^0 is increased in increments of 500 cm^{-1}, the energy to which the eigenvalues are converged increases by almost 500 cm^{-1}. This is an ideal situation for any variational calculation; it is the result of a basis set where the only couplings are those between nearly degenerate states. Similar convergence was found by Ramesh et al. for CHF$_3$.[33]

Having verified the convergence of the variational part of the calculation, we can now test the convergence with respect to the order of the perturbation theory. In Figure 3, we plot the difference between eighth- and sixth-order results as a function of excitation energies. One can see that the convergence is good up to 7000 cm^{-1} of excitation for both the δ set of coordinates and the polyspherical coordinates, with the convergence being slightly better for the former. Focusing on just the overtone states shown in Figure 4, we see that at slightly higher energies the discrepancy between the coordinates is greater with the poly-spherical results having E(eighth order) $-$ E(sixth order) values almost as large as 90 cm^{-1} for the overtone of the out-of-plane bend.

V. Effect of the PES Fit on the Accuracy of the Spectrum

In this section, we further examine the quality of our fits of the Kato potential.[58] It is essential to quantify the accuracy of a fit. An easy way to do this is to plot the differences between the two surfaces. Such an analysis is not so trivial when the number of degrees of freedom increases. One can readily compare 2D slices as we have done in Figure 1. It is, however,

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Figure 4. Difference between eighth- and sixth-order perturbative energies, E(eighth order) $-$ E(sixth order) plotted as a function of the corresponding excitation energy (in cm^{-1}) of overtones states with excitation energies less than 8000 cm^{-1} when the PES is fit with (a) the δ set and (b) the ϕ set of coordinates. Only states of A′ symmetry are included.

Figure 5. Energy difference ($E_{\text{originalPES}} - E_{\text{fittedPES}}$) expressed in cm^{-1}. The top and bottom panels use the fits obtained with the ϕ and δ sets of the coordinates. The energies are provided by the JW variational method, and only states $|v_1, ..., v_6\rangle$ such that $v_i \leq 4$ are included in the comparison.
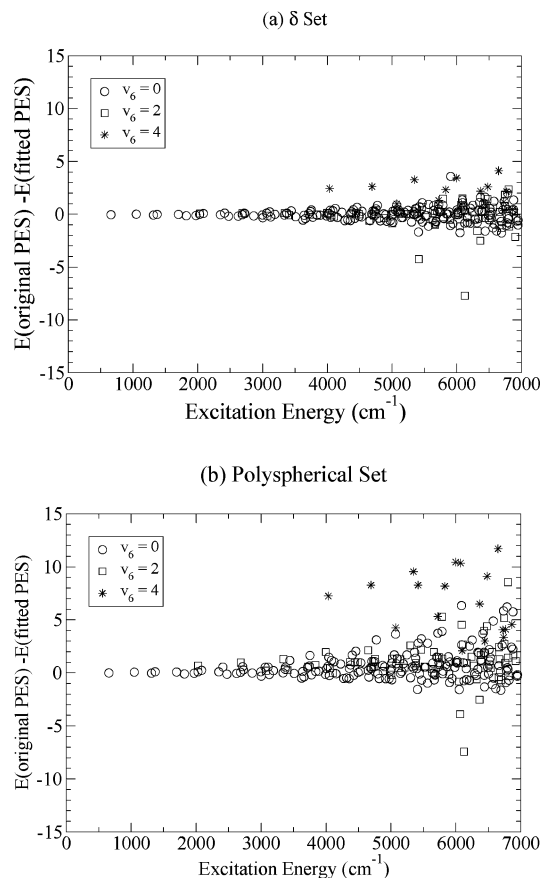
not easy from the comparison to estimate the consequence of small differences on excitation energies and on the eigenstates. For this reason, we will estimate the error generated by the polynomial fit by comparing eigenvalues and eigenvectors for the surfaces.

The excitation vibrational spectrum has been computed with the JW method described in section III with three different PESs: the original global one developed by Kato[58] which constitutes in this study the reference PES and the fitted expressions of this reference PES by using either the polyspherical set (the ϕ set) or the δ set of coordinates.

Figure 5 represents the error in the energies of A′ states $|v_1, ..., v_6\rangle$ such that $v_i \leq 4$ generated by the fit using either the ϕ set or δ set of coordinates; Figure 6 provides the same information for the A′ overtones states $|nv_i\rangle$ up to 8000 cm^{-1}. First, it is remarkable that these rather simple fits provide accurate energies for states with small excitation in the out-of-plane mode and even for highly excited overtones of the in-plane modes. The only significant errors are observed for states with large excitation in the out-of-plane modes.

Focusing specifically on these states, we compare expressions of the eigenstates associated with the fifth and seventh out-of-plane overtones. In Table 3, we compare expansion coefficients $c_{v_1, ..., v_6}$ for select wave functions describing the out-of-plane bending motion.

$$|nv_6\rangle = \sum_{v_1, ..., v_6} c_{v_1, ..., v_6} |v_1, ..., v_6\rangle^o \qquad (8)$$

Table 3 provides the main projections of these eigenstates onto the working basis set. This table demonstrates that the description of the overtone states is similar for all three PESs used. This result is crucial; it shows that our fitted PES, which provides energies with errors larger than the average level spacing, provides a reasonably correct description of the eigenstates. That means, for instance, that the dynamical behavior, that is, the vibrational energy flow through the molecule, should be very similar whatever the PES used up to 8000 cm^{-1} of excitation energy.

VI. Comparison of CVPT Perturbative and JW Variational Results

The excitation spectrum obtained after a sixth- or eighth-order perturbative treatment is now compared to the spectrum obtained with the variational JW method. This comparison allows us to quantify the accuracy of the spectrum obtained with CVPT. One has to remember that the error of the variational calculation generated by the finite dimension of the basis set can be estimated to 0.1 cm^{-1} for energies near 3000 cm^{-1} and less than about 3 cm^{-1} near 8000 cm^{-1}. It should be possible to improve this accuracy by performing a specific calculation in an ideally adapted basis for the 300 states calculated in this study. However, such an accuracy is sufficient because the inherent error of the PES for highly excited energies is larger than this quantity.

We first focus on the spectrum obtained with the PES fitted with the δ-set of coordinates. Figure 7 compares the variational energies of combination states ($|v_1, ..., v_6\rangle$ with $v_i \leq 4$) with
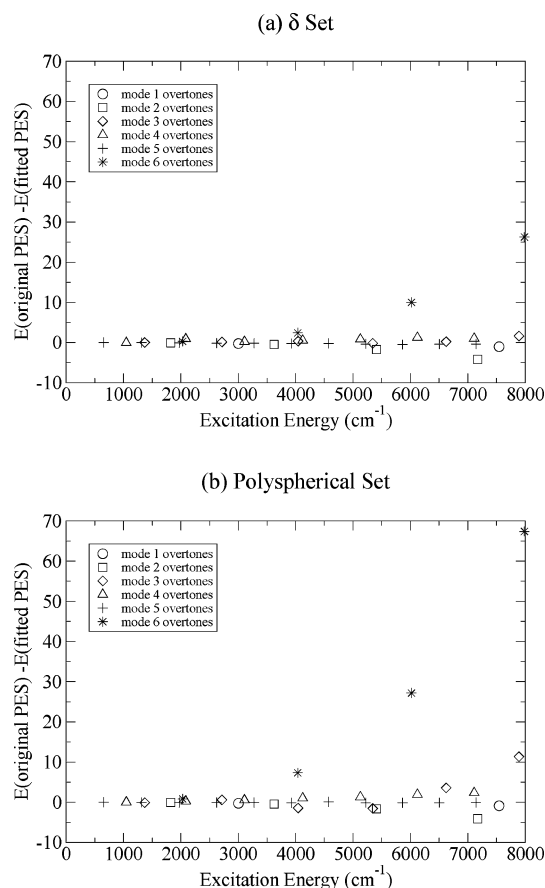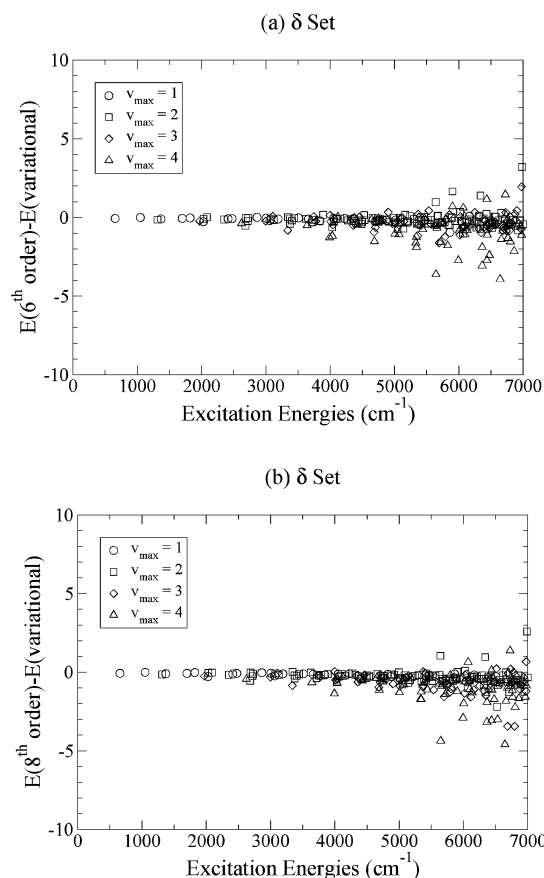
Figure 6. Energy difference ($E_{originalPES} - E_{fittedPES}$) expressed in cm^{-1} for A′ overtone states $|nv_i\rangle$. The top and bottom panels use the fits obtained with the δ and ϕ sets of the coordinates, respectively. The energies are provided by the JW variational method.

Figure 7. Energy difference ($E_{CVPT} - E_{variational}$) expressed in cm^{-1} for $|v_1, ..., v_6\rangle$ such that $v_i \leq 4$ when the PES is fit with the δ set of coordinates. The states are labeled by the sum $v_{max} = \sum_i v_i$: (a) CVPT results at sixth order and (b) CVPT results at eighth order.

TABLE 3: Absolute Value of the Coefficient $c_{v_1,...,v_6}$ Larger than 0.15 for the Overtones $|6v_6\rangle$ and $|8v_6\rangle$ Expressed in the Zero-Order Working Basis Set of Eq 8^a

state	original PES	δ fit	polyspherical fit
$6v_6$	$E = 6018.4$	$E = 6008.4$	$E = 5991.24$
	$0.17\ |6_4\rangle^0$	$0.17\ |6_4\rangle^0$	$0.17\ |6_4\rangle^0$
	$0.77\ |6_6\rangle^0$	$0.77\ |6_6\rangle^0$	$0.77\ |6_6\rangle^0$
	$0.14\ |4_16_8\rangle^0$	$0.16\ |4_16_8\rangle^0$	$0.15\ |4_16_8\rangle^0$
	$0.22\ |3_16_6\rangle^0$	$0.23\ |3_16_6\rangle^0$	$0.23\ |3_16_6\rangle^0$
	$0.18\ |2_16_4\rangle^0$	$0.19\ |2_16_4\rangle^0$	$0.20\ |2_16_4\rangle^0$
	$0.28\ |1_16_4\rangle^0$	$0.28\ |1_16_4\rangle^0$	$0.27\ |1_16_4\rangle^0$
	$0.15\ |1_16_6\rangle^0$	$0.15\ |1_16_6\rangle^0$	$0.15\ |1_16_6\rangle^0$
$8v_6$	$E = 7984.9$	$E = 7958.65$	$E = 7917.52$
	$0.25\ |6_6\rangle^0$	$0.24\ |6_6\rangle^0$	$0.25\ |6_6\rangle^0$
	$0.64\ |6_8\rangle^0$	$0.64\ |6_8\rangle^0$	$0.63\ |6_8\rangle^0$
	$0.17\ |4_16_8\rangle^0$	$0.16\ |4_16_8\rangle^0$	$0.16\ |4_16_8\rangle^0$
	$0.24\ |3_16_8\rangle^0$	$0.25\ |3_16_8\rangle^0$	$0.25\ |3_16_8\rangle^0$
	$0.20\ |2_16_6\rangle^0$	$0.22\ |2_16_6\rangle^0$	$0.26\ |2_16_6\rangle^0$
	$0.30\ |1_16_6\rangle^0$	$0.29\ |1_16_6\rangle^0$	$0.28\ |1_16_6\rangle^0$
	$0.15\ |1_16_8\rangle^0$	$0.15\ |1_16_8\rangle^0$	$0.15\ |1_16_8\rangle^0$

^{a} Absolute values are given since the signs cannot be compared. Here, we use the notation, for example, $|4_16_8\rangle^0$ to represent the state $|0, 0, 0, 1, 0, 8\rangle^0$.

the perturbative energies obtained with a sixth- and eighth-order perturbative treatment, respectively. These results demonstrate that the CVPT convergence is excellent. The quality of the spectrum obtained is very good even after the sixth-order perturbative treatment. The main disagreement between the sixth and eighth orders is obtained for states with large excitation in the out-of-plane mode. When the energy obtained by CVPT is slightly smaller than the variational energy, one can think that

the CVPT value is more accurate because a variational calculation in a larger basis should provide slightly smaller energies. It is not a rule but is usually observed when the state is not too strongly coupled to another via an anharmonic resonance. When the CVPT energy is slightly larger than the variational energy, one can assume that the variational value is more accurate. This latter case does not occur often (few points correspond to this case). Consequently, the accuracy of the energies provided by CVPT is impressive. One can also notice that the differences between the variational and perturbative energies are not significant: this error is smaller than the error generated by the inherent inaccuracy of a PES.

Figure 8 focuses on overtones states up to 8000 cm^{-1}. This figure reveals that the in-plane overtones are very accurately obtained after sixth-order treatment and show slow convergence of highly excited out-of-place overtones. This is consistent with Figure 2 which shows that the convergence of the perturbative treatment is slow for states with large excitation in the out-of-plane mode. However, the result obtained after an eighth-order perturbative treatment is satisfactory.

One can now focus on the spectrum obtained with the fit performed with the polyspherical coordinates (cf. Figures 9 and 10). CVPT converges more slowly with this ϕ set of coordinates. It is not trivial to predict why the δ set of coordinates seems to be more adapted to describe this system. One possible reason is that the singularities inherent in using normal coordinates occur at lower energies for the ϕ set than the δ set. Specifically, the out-of-plane ϕ coordinate is ill-defined if $\overrightarrow{CO} \times \overrightarrow{CH} = 0$ or $\overrightarrow{CO} \times \overrightarrow{CF} = 0$, while the δ set is defined even when the atoms are collinear. In either coordinate set, however, an eighth-order

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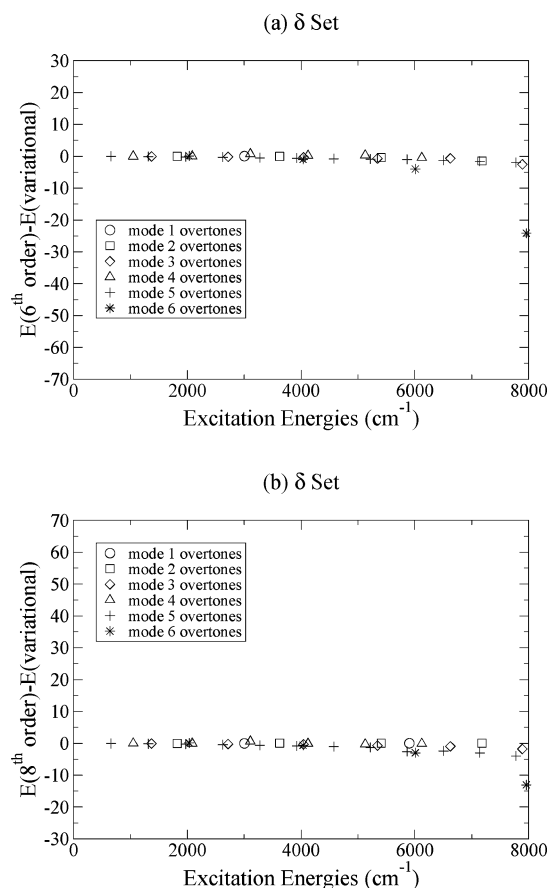
Figure 8. Energy difference ($E_{CVPT} - E_{variational}$) expressed in cm^{-1} for the overtones states $|nv_i\rangle$ up to 8000 cm^{-1} when the PES is fit with the δ set of coordinates. The states are labeled by the sum $v_{max} = \sum_i v_i$: (a) CVPT results at sixth order and (b) CVPT results at eighth order.

Figure 9. Energy difference ($E_{CVPT} - E_{variational}$) expressed in cm^{-1} for $|v_1, ..., v_6\rangle$ such that $v_i \leq 4$ when the PES is fit with the ϕ set of coordinates: (a) CVPT results at sixth order and (b) CVPT results at eighth order.
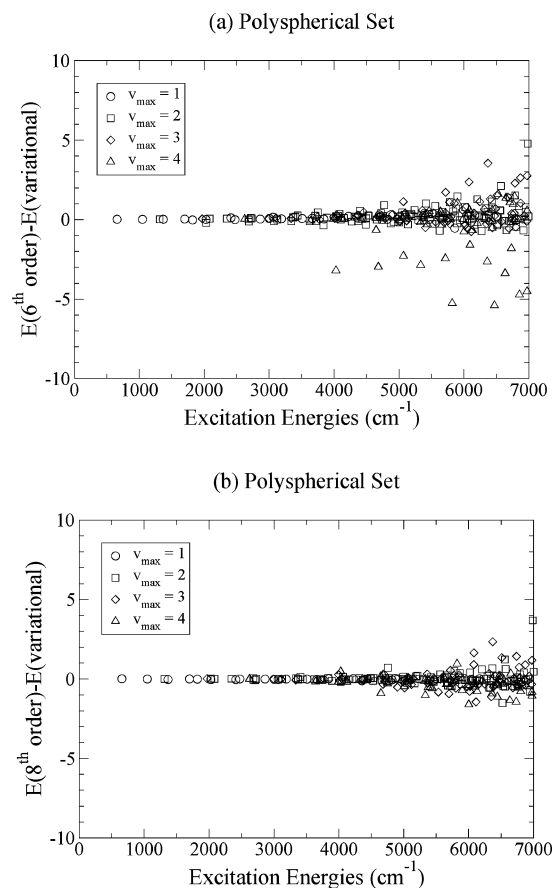
treatment provides an excellent spectrum when the out-of-plane mode is not too excited.

In summary, the above comparisons demonstrate the great accuracy of the CVPT approach up to 8000 cm^{-1}. CVPT results are least accurate for states with a large excitation in the out-of-plane mode. For these states, the convergence is slower with the polyspherical set of coordinates. This point is consistent with Figure 4 which reveals that the convergence of the perturbative treatment is slower for states with large excitation in mode 6.

VII. Conclusion and Perspectives

This study has quantified the accuracy of eigenvalues obtained via the perturbative CVPT method by comparing them to those obtained with the variational JW method. The results demonstrate the great accuracy of CVPT for calculating both combination states and overtones states up to 8000 cm^{-1}. CVPT is almost always faster than a variational method and as accurate for a moderately excited part of the spectrum. A notable caveat is that one must compare successively higher orders of the perturbation theory and test for convergence. It is important to mention that the labels of the states studied are nearly identical for the two methods even while strong anharmonic resonances couple multiple zero-order states. This point is not trivial because the space in which the Hamiltonian is diagonalized is different in these two methods.

HFCO was chosen for this study because this molecule is, a priori, not ideally suited to treatment by CVPT. First, it is not possible to define a quantum number $N = \sum_{i=1}^{6} c_i v_i$ to define

polyads of states; second, there is a relatively low dissociation energy. Nonetheless, the agreement found here is similar to the results obtained by Ribeiro[72] in a preliminary study devoted to H$_2$CO and using the PES fitted by Sibert and co-workers with CVPT.[30] In that study, it was demonstrated that the energies provided by the JW method always converge to the CVPT value up to 9500 cm^{-1}. However, H$_2$CO is a rather simple system to treat by CVPT because polyads of states are easy to define and dissociation occurs at higher energies. Consequently, the HFCO system studied here provides a more rigorous test of the method than earlier studied systems where comparisons were made to variational results.

This study examined the error that is introduced when working with a PES that has been fit to a polynomial form; this being a requirement of CVPT. To quantify this error, we compared variational results from the JW method for a global surface and fits to this surface. We found that the error generated by the polynomial fit is very limited and smaller than the inherent inaccuracy of a PES for all the states moderately excited in the out-of-plane mode. The out-of-plane mode should require more attention and a more sophisticated fit. We also noted that the basis set expansion coefficients of the eigenstates describing the highly excited out-of-plane overtones are not very sensitive to the accuracy of the fit. This point is important and reveals that the fitted expressions correctly represent the main intermode couplings for this system. This trend has also been observed in a recent study using the MCTDH method,[73,74] a method that also requires a fit to the PES in order to provide the time evolution of wave packets. It has been shown recently that the energy flow through the system is not very sensitive to the

(a) Polyspherical Set

(b) Polyspherical Set
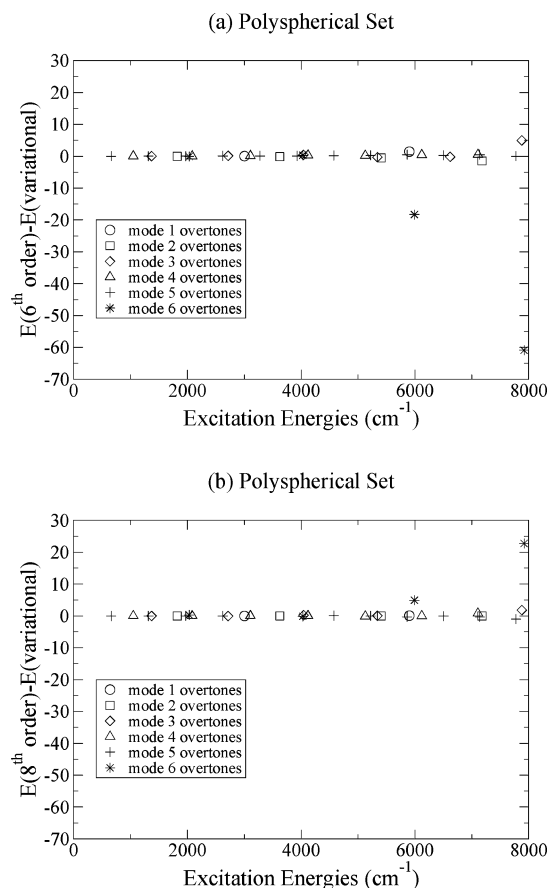
Figure 10. Energy difference ($E_{CVPT} - E_{variational}$) expressed in cm^{-1} for the overtones states $|nv_i\rangle$ up to 8000 cm^{-1} when the PES is fit with the ϕ set of coordinates: (a) the CVPT result is sixth order, and (b) the CVPT result is eighth order.

accuracy of the fit.[75] In addition to examining the error introduced by using a polynomial fit to the potential, we quantified the influence of the choice of the set of coordinates used to describe the system: this role is not decisive but is not negligible. In our case, the results obtained with CVPT when the δ coordinates are used are more accurate and easier to obtain than when the polyspherical coordinates are adopted. This trend is not trivial to predict. However, the eighth-order CVPT results are very satisfactory and similar whatever set of coordinates is used.

It is important to mention that these two methods (JW and CVPT) are general and can be applied to any semirigid system. The JW method limitation comes from the dimension of the working basis set. A preliminary SCF[27,76,77] or MCSCF[26] treatment should decrease the dimension of the working basis set and allows us to treat larger systems. The CVPT method limitation comes from the necessity of not being able to remove couplings between nearly degenerate states. The resulting Hamiltonian may be too large to diagonalize with traditional methods. In future work, we plan to use the Davidson scheme to diagonalize such Hamiltonians, thus allowing us to extend the perturbative approach to study highly excited states of larger molecules.

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